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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US00/01929 <b>(22) International Filing Date:</b> 27 January 2000 (27.01.00)  <b>(30) Priority Data:</b> 09/250,799 17 February 1999 (17.02.99) US  <b>(71) Applicant:</b> CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US).  <b>(72) Inventors:</b> CUTLER, Willard, A.; 6 Churchill Place, Big Flats, NY 14814 (US). TURNS, Jennifer, M.; 1 Jacob Drive, Painted Post, NY 14870 (US).  <b>(74) Agent:</b> HERZFELD, L., Rita; Patent Dept., SP TI 3-1, Corning Incorporated, Corning, NY 14831 (US).		<b>(81) Designated States:</b> CN, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVED METHOD OF MAKING MULTICELLULAR FILTERS  <b>(57) Abstract</b>  A method of plugging honeycomb cells (12) involves providing a honeycomb having an inlet end and an outlet end and a multiplicity of cells (12) extending from inlet end to outlet end, and introducing the sealant material (16) into pre-selected honeycomb cell openings by capillary action to form a plug on said pre-selected cell openings. The sealant can also be thermoplastic polymer preform having sections corresponding to the cell openings on a given surface of a honeycomb. The preform is positioned on the honeycomb surface having the pre-selected cell openings so that the preform is inserted into the pre-selected cell openings. The pre-selected cell openings are heated to allow the preform to deform into a thermoplastic sealing material and bond to inside walls of the pre-selected cell openings, to produce a plugged honeycomb with plugs securably positioned into the selected cell openings.		

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IMPROVED METHOD OF MAKING MULTICELLULAR FILTERS

This invention relates to an improved plugging method for making multicellular filters.

5

Background of the Invention

Multicellular structures such as honeycombs find use as filters for fluids. By plugging alternate cells or channels of a honeycomb, fluid flow is forced through the cell walls, allowing the wall to perform particulate  
10 filtration. This through-the-wall flow pattern takes advantage of the high surface area/volume ratio of the honeycombs. These honeycomb filters, in particular, ceramic honeycombs, have been used extensively for gas  
15 phase filtration, such as in the diesel particulate filtration application, due to their high temperature capability.

Conventional plugging methods, such as for example applying a removable mask and forcing the plugging  
20 material into the unmasked cells, then removing the mask, or injecting the plugging material directly into the cell to be plugged, are very slow processes. The other disadvantage of some of these methods is their inability to adapt to plugging higher cell density structures (>200  
25 cells/in<sup>2</sup>).

Honeycombs have not as yet found wide use as liquid filters. As many liquid filtration needs do not require plugging with a high temperature material, the methods and possibilities for plugging honeycombs for such applications require different solutions. New solutions to the plugging problems of honeycombs in liquid filtration should be applicable regardless of whether the honeycomb is ceramic, carbon, polymer, or some combination of these. All filtration applications require that the plugs in honeycombs must exhibit no bypass (fluid leakage around the plug) to maintain particulate, pollutant, and parasite removal properties of the filters.

The present invention sets forth a variety of plugging methods for plugging honeycombs for use in fluid filtration. The methods fulfill the requirements of completely plugging designated cell channels to a controlled depth, to prevent fluid leakage around the plug.

#### Summary of the Invention

In accordance with one aspect of the invention, there is provided a method of plugging honeycomb cells involves providing a honeycomb having an inlet end and an outlet end and a multiplicity of cells extending from inlet end to outlet end, and introducing the sealant material into pre-selected honeycomb cell openings by capillary action to form a plug on said pre-selected cell openings.

In accordance with another aspect of the invention, the sealant can be thermoplastic polymer preform having sections corresponding to the cell openings on a given surface of a honeycomb, the sections corresponding to the openings that are to be plugged have thermoplastic sealing material. The sealing material has dimensions to allow it to fit securably into honeycomb cell openings to be

plugged. The preform is positioned on the honeycomb surface having the pre-selected cell openings so that the sealing material is inserted into the pre-selected cell openings. The pre-selected cell openings are heated to allow the thermoplastic sealing material to deform and bond to inside walls of the preselected cell openings, to produce a plugged honeycomb with plugs securably positioned into the selected cell openings.

#### Brief Description of the Drawings

Figures 1 and 1a are schematic diagrams showing plugging selected honeycomb cells by capillary action.

Figures 2 and 2a are schematic diagrams showing sealant applied as a continuous line in a diagonal across the cross section of the honeycomb.

Figure 3, 3a, 3b, 3c, are schematic diagrams showing honeycomb cells being plugged by masking the cells that are to be ultimately left open with a fugitive material, which is removed after the cells to be plugged are filled with sealant by capillary action.

Figures 4 and 4A are schematic diagrams showing honeycomb cells being plugged by masking the cells, similar to Figures 3-3c above, but the mask is in the form of a single piece.

Figures 5 and 5a are schematic diagrams showing plugging honeycomb cells with a wedge-shaped sealant material.

#### Detailed Description of the Invention

This invention relates to methods of plugging honeycombs to produce a filter having wall flow, for filtration of fluids. More specifically, this invention relates to various methods of applying sealant to honeycomb cells to a controlled depth and pore

penetration, within the cells, to form plugs. The sealant forms a plug that is integral with the cell wall and wall pores.

5 The honeycombs can be made of any material such as ceramic, metal, polymer, carbon or activated carbon, glass, glass-ceramic, or combinations of these.

10 The honeycombs can have any cell density, but cell densities usually range from 235 cells/cm<sup>2</sup> (about 1500 cells/in<sup>2</sup>) to 1.5 cells/cm<sup>2</sup> (about 10 cells/in<sup>2</sup>). They can have variable wall thicknesses, but wall thicknesses range typically from about 0.1 to about 1.5 mm (about 4 to about 60 mils). This invention is especially useful for the more dense honeycombs of 31 cells/cm<sup>2</sup> (200 cells/in<sup>2</sup>) or greater.

15 The sealant is selected depending on the material of the honeycomb. It must be able to form a strong chemical, mechanical, or frictional bond with the cell surface of the honeycomb so that there is no leakage around the plug that is formed. Some examples of typical sealing or  
20 plugging materials, although it is to be understood that the invention is not limited to these, are polymeric materials such as epoxies, silicones, waxes, thermoplastic polymers, and inorganic/organic mixes such as ceramic/polymer mixes, etc.

25 There are several ways in which the plugging can be done.

30 In one embodiment, the pre-selected cells are plugged by capillary action with liquid-based sealant. The top of the cell(s) opening(s) to be plugged are placed in contact with the sealant material and the sealant is allowed to be pulled into the cell(s) to some desired depth by capillary forces (as opposed to forcing the sealant into the cell by injection, applied pressure, or some other traditional

method). This invention does not require precise placement of the sealant in the center of the cell(s) to be plugged. As long as the majority of the sealant ends up on top of the required cell, capillary action pulls the sealant into the cells and overcomes the misalignment. The sealant can be applied to discrete cells, or it can be applied directionally, in a continuous line pattern, such as diagonally. The latter technique is more efficient because it expedites sealing of a large number of cells. The degree of penetration of sealant into the cell is determined by the size of the cell, viscosity of the sealant, wetting characteristics of the sealant with the cell, etc. Depending on the size of the cell, the characteristics of the sealant can be adjusted to yield desired plugging depth and pore penetration. For example, plug penetration depth can be controlled by sealant viscosity. The higher the sealant viscosity, the shorter the plug depth. Lower viscosity sealants can also produce shorter plug depths if used in conjunction with an ultraviolet (UV) curing agent initiator in the sealant and exposing the part to UV radiation.

In another embodiment, the entire end of the honeycomb is subjected to the sealing material. Each of the cells are filled to a desired depth (vs. completely filling the entire cell channel) as the sealing material wicks into the cells. The sealed honeycomb end is then removed from the sealant and rods of diameter less than the cell size, arranged in a pattern desired for the open cells, are plunged into the honeycomb. The high viscosity sealant attaches itself to these rods and the sealant is removed from the cell as the rods are withdrawn from the honeycomb. The process is repeated to produce the opposite pattern on the other side of the honeycomb.

In another embodiment, cells that are to be left open are masked with a removable or fugitive masking material. The entire face of the honeycomb is exposed to the sealant which fills the unmasked cells by capillary action. Especially suited as masking material for this technique, although it is to be understood that the invention is not limited to such, are silicones that are removable under the processing conditions, low melting waxes, and thermoplastic elastomers. The melting point for the waxes used as fugitive masking materials needs to be low enough that the epoxy or other plugging material is not damaged, but that the low melting point compound can be removed. Especially suited as sealant is a two-part epoxy. Each cell density will require a different viscosity - the higher, the cell density the lower the viscosity. The fugitive masking material is then removed by heating.

In still another embodiment, the cells of a honeycomb to be plugged are plugged at once with a pre-formed mask. The plugs of the mask which will ultimately be the plugs of the honeycomb, are made of previously described plugging material e.g. molded thermoplastic elastomer, wax, or epoxy with only the epoxy skin being cured either by UV or heat. The mask is physically pressed into the honeycomb to plug all of the desired cells at once. In the case of a thermoplastic elastomer or wax, insertion into a honeycomb that is at least hot enough to partially melt the sealant plug of the mask, results in a strong mechanical bond without leakage. In the case of an epoxy sealant plug, the mechanical action of pressing breaks the cured skin of the plugs allowing some flow of the uncured epoxy resulting in formation of a chemical bond.

To more fully illustrate the invention, the following non-limiting examples are presented with accompanying drawings.

Use of capillary action to plug cellsExample 1

5            Figures 1 and 1a illustrate honeycomb cells being put  
in contact with a sealant and allowing capillary forces to  
pull the sealant into the cell. Figure 1 is a schematic  
diagram showing the lengths of honeycomb cells (12). Cell  
walls are shown as (14). Sealant 16) is placed at the  
10           opening of a cell or cells. Figure 1a is similar to Figure  
1, but shows the sealant (16a) being subjected to  
capillary forces that pull the sealant into the cell.  
Besides being applied to multiple discrete cells as shown  
in Figure 1, the sealant can be applied in a pattern, such  
15           as a diagonal, to expedite the process. Figure 2 is a  
schematic of a cross section of honeycomb cells (20), with  
sealant (22) applied as a continuous line in a diagonal  
across the cross section of the honeycomb. Figure 2A is  
similar to Figure 2 but shows sealant plugging (22a) in  
20           the cells (20) after the sealant is allowed to plug the  
cells by capillary action. One suitable sealant especially  
in the above described embodiments is a two part epoxy  
having a viscosity of e.g. about 250,000 cps.

Example 2

A 200 cell/in<sup>2</sup> porous ceramic honeycomb with about 0.028" thick walls with fine porosity (<10 micrometers) was plugged diagonally using a two-part with a viscosity of about 200,000 cp. The epoxy bead was continually dispensed in a diagonal line pattern using a pneumatic syringe, guided by hand. The opposing diagonal line pattern was placed on either side of the honeycomb and the plugged part was subjected to about 70°C for about 1 hour. The final, cured plug depth was about 2 mm.

Example 3

A 300 cell/in<sup>2</sup> porous carbon honeycomb with about 0.015" walls with fine porosity (<2 micrometers) was plugged in a diagonal pattern using a two part epoxy with a viscosity of about 100,000 cp. The epoxy bead was continually dispensed in a diagonal line pattern using a pneumatic syringe, guided by hand. The opposing diagonal line pattern was placed on the other side of the honeycomb and the plugged part was subjected to about 70°C for about 1 hour. The final, cured plug depth was about 2 mm.

Example 4

A 400 cell/in<sup>2</sup> porous ceramic honeycomb with about 0.010" thick walls with fine porosity (<3µm) was plugged diagonally using a two-part epoxy with a viscosity of about <40,000 cp. The epoxy bead was continually dispensed using a pneumatic syringe, guided by a computer controlled x-y-z table. The opposing diagonal line patterns were placed on either side of the honeycomb and subjected to about 70°C for about 1 hour. The final, cured plug depth was < 3 mm.

Example 5: Use of capillary action combined with cell masking

Figures 3, 3a, 3b, and 3c illustrate the principle of masking the cells that are to be ultimately left open, with a fugitive or removable masking material, and then subjecting the whole face of the honeycomb to the sealant and allowing the unmasked cells to be filled by capillary action. Figure 3 is a schematic showing the lengths of cells (32) with mask (33), and cell walls (34). Figure 3a shows the cells (32) with mask (33), and cells (32a) being dipped into a container (36) having sealant (38). Figure 3b shows the resulting honeycomb cells (32) with masks (33) and cells (32a) with sealant plugs (38a). The mask is then removed such as by heating. Figure 3c is a schematic showing honeycomb cells having sealant after the masking material is removed. One suited material for masking the cells that are to remain open is wax, while a two part epoxy having a viscosity of e.g. about 150,000 cp is utilized as the sealant. The viscosity is dependent on the cell geometry.

Example 6: Use of a pre-formed mask with mechanical attachment

All the cells of a honeycomb to be plugged can be plugged at once with use of a pre-formed mask. The pre-formed mask can be made of a molded thermoplastic elastomer or wax or related material and would be physically pressed into the honeycomb to plug all of the desired cells at once as shown in Figure 4. Figure 4 is a schematic diagram showing the lengths of honeycomb cells (42) and cell walls (44), and mask (46) having plugs (48) which are inserted into the honeycomb cells at both ends. The plugs are shown alternately plugging the cells.

Application of heat either to the honeycomb or to the mask and use of wedge-shaped plugs result in an integral mechanical seal with the porous honeycomb walls. Figure 5 is a schematic diagram of a wedge-shaped plug (52), about to be inserted into a honeycomb cell (54) having porous walls (56) with pores shown as (58). Figure 5a shows the cell after plugging with the plug (52a) integrally sealed to the cell wall.

10 Example 7: Use of a pre-molded mask with chemical attachment

All the cells to be plugged can be plugged at one time with use of a pre-molded mask that would be made of a molded epoxy with both UV and heat-curable components. A thin skin can be induced using UV radiation allowing the material to retain its shape. The pre-form is physically pressed into the honeycomb as described in Example 6. The mechanical action of the pressing breaks the skin of the wedge-shaped plugs allowing some flow of the uncured epoxy into the cells and along the cell walls. The entire pre-molded mask can then be heat cured, allowing the formation of a chemical bond between the epoxy and the cell walls.

Example 8: Use of plugging, followed by clearing of plugs

25 A 100 cell/in<sup>2</sup> porous ceramic honeycomb with about 0.028" walls with fine porosity (5  $\mu$ m) was dipped (1/4") into two-part epoxy with a viscosity of about <100,000 cp for < 1 min. The honeycomb was removed from the epoxy and a wooden rod was inserted and removed from the cells to be cleared. The honeycomb was subjected to about 70°C for about 1 hour. The final, cured plug depth was about 3 mm.

It should be understood that while the present invention has been described in detail with respect to

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certain illustrative and specific embodiments thereof, it should not be considered limited to such but may be used in other ways without departing from the spirit of the invention and the scope of the appended claims.

What is claimed is:

1. A method of plugging honeycomb cells, the method comprising;

5 a) providing a honeycomb having an inlet end and an outlet end and a multiplicity of cells extending from inlet end to outlet end;

b) providing sealant material;

10 c) introducing the sealant material into pre-selected honeycomb cell openings by capillary action to form a plug on said pre-selected cell openings.

15 2. A method of claim 1 wherein the sealant is selected from the group consisting of epoxy materials, silicones, cements, ceramics, urethanes, thermoplastics, and combinations thereof.

20 3. A method of claim 2 wherein the sealant is epoxy material.

4. A method of claim 1 wherein the sealant is introduced into the pre-selected cell openings by applying sealant in a continuous line pattern across a plurality of pre-selected cell openings; and allowing said sealant to be  
25 drawn into said plurality of cell openings.

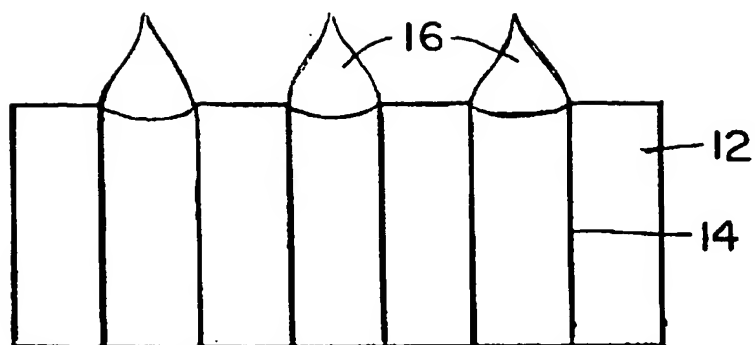
5. A method of claim 4 wherein the sealant is epoxy material.

30 6. A method of claim 4 wherein the sealant contains a ceramic filler which, on sufficiently high heat treatment, is essentially all ceramic.

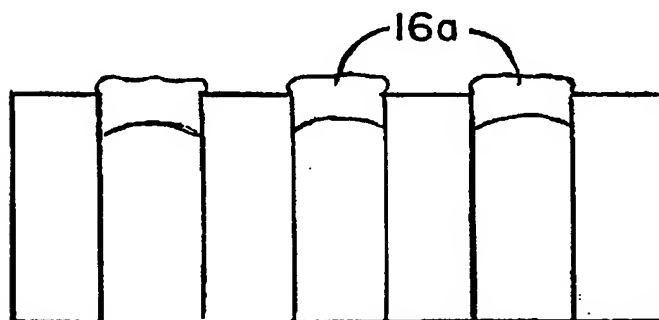
7. A method of claim 1 wherein the entire end of the honeycomb is subjected to the plugging material which wicks into all of the cells and where selected cells have rods inserted and removed after the cells have been filled to clear the cells.
8. A method of claim 7 wherein the rods are wooden and disposable.
9. A method of claim 1 wherein before sealant is introduced into said pre-selected cell openings, the cell openings that are to be unplugged are masked with fugitive material, and wherein after sealant is applied to the pre-selected cell openings, said fugitive material is removed.
10. A method of claim 9 wherein the fugitive material is selected from the group consisting of low-melting waxes, and thermoplastics.
11. A method of plugging honeycomb cells, the method comprising;
- a) providing a honeycomb having an inlet end surface and an outlet end surface, and a multiplicity of cells defining cell walls, and extending from inlet end surface face to outlet end surface and opening on said surfaces, and pre-selecting cell openings to be plugged;
  - b) providing sealant as a thermoplastic polymer preform having sections corresponding to the cell openings on a given surface of said honeycomb, wherein the sections corresponding to the openings that are to be plugged have thermoplastic sealing material, the sealing material having dimensions to allow it to fit securably into honeycomb cell openings to be plugged; and

c) positioning said preform on the honeycomb surface having said pre-selected cell openings so that said thermoplastic sealing material is inserted into said pre-selected cell openings, said pre-selected cell openings being heated to allow said thermoplastic sealing material to deform and bond to inside walls of the pre-selected cell openings, whereby a plugged honeycomb is produced having plugs securably positioned into said selected cell openings.

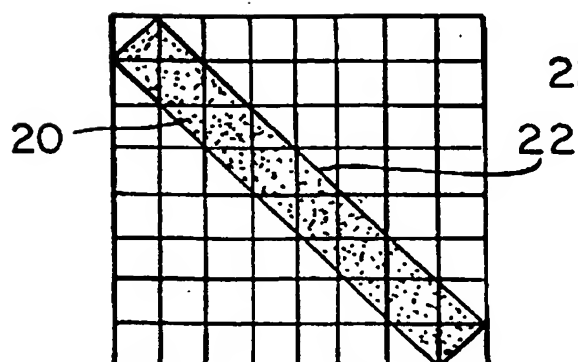
12. A method of claim 11 wherein the sealant is an epoxy which has an outer cured skin covering uncured material inside the cured skin, and wherein the skin is broken as the preform is inserted into said pre-selected cells, allowing the uncured material to plug said pre-selected cells.



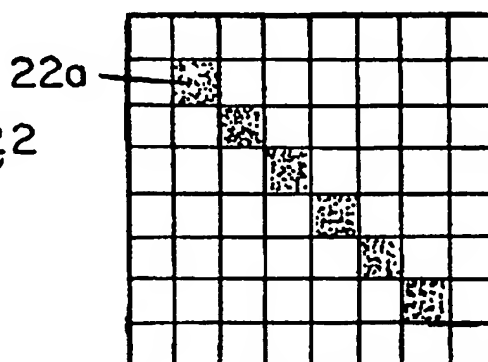
*Fig. 1*



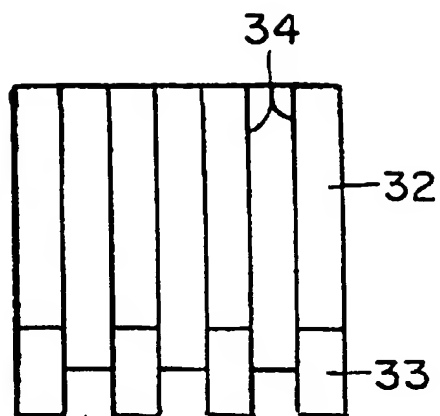
*Fig. 1a*



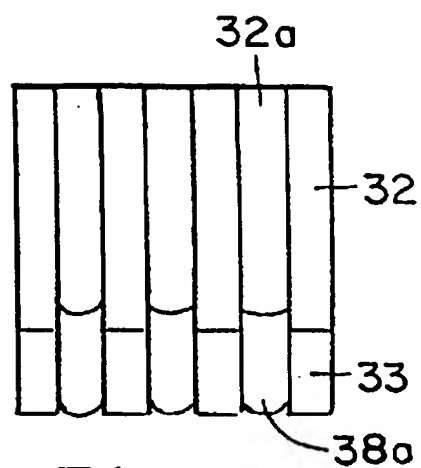
*Fig. 2*



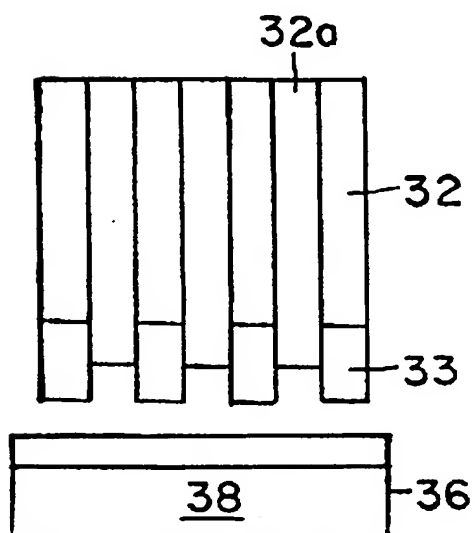
*Fig. 2a*



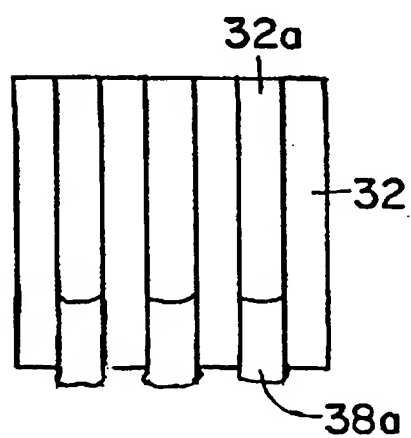
*Fig. 3*



*Fig. 3b*

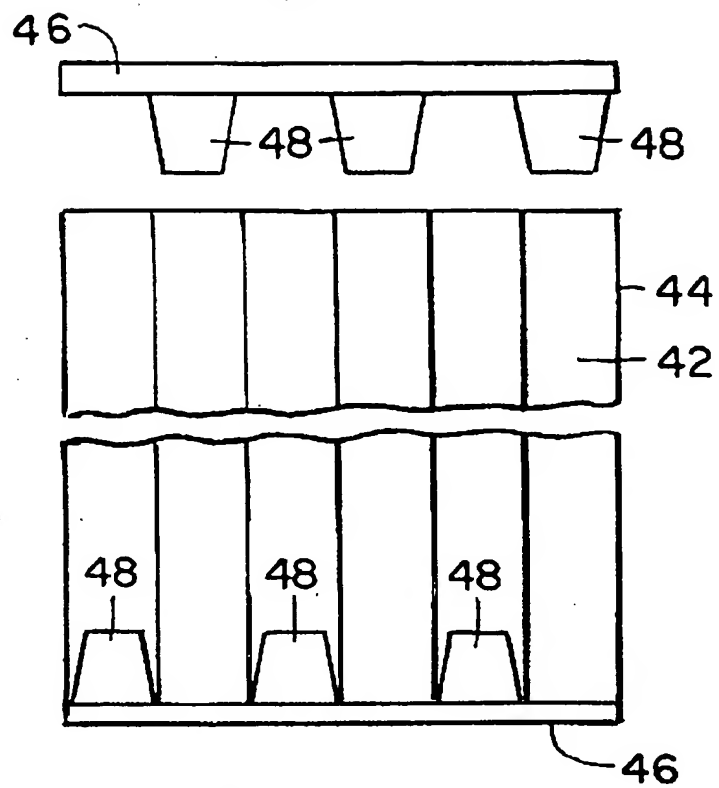


*Fig. 3a*

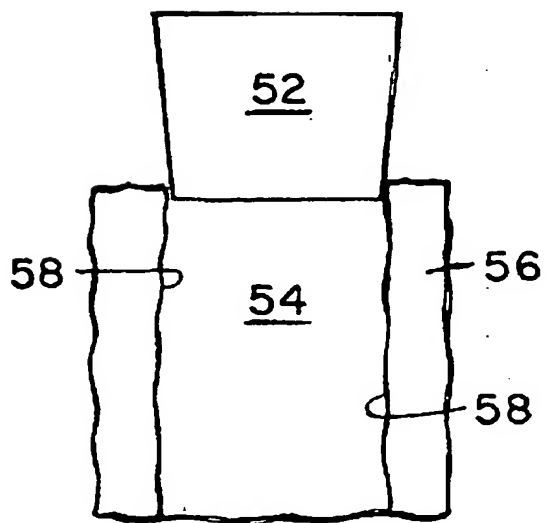


*Fig. 3c*

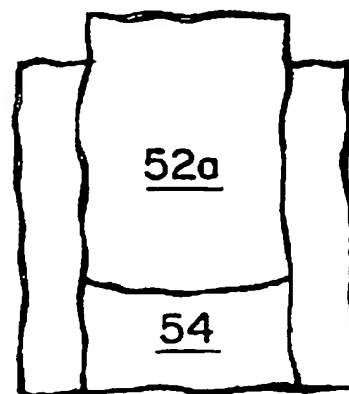
3/3



*Fig. 4*



*Fig. 5*



*Fig. 5a*

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/01929

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B28B 1/28; B29C 31/08

US CL :264/156, 267, 320

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/154, 156, 259, 267, 313, 317, 320

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

BRS search term: honeycomb, filter

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,364,573 A (NOKY) 15 November 1994, see entire document.	1-6
Y,P	US 5,997,746 A (VALASKOVIC) 07 December 1999, col. 5, lines 44-67.	1-10
Y	US 5,433,904 A (NOKY) 18 July 1995, see entire document.	1-8, 11, 12
Y	US 4,793,920 A (CORTES et al) 27 December 1988, col. 4, lines 59-68.	1-10
Y	US 4,411,856 A (MONTIERTH) 25 October 1983, see entire document.	1-3, 9-10
A	US 5,766,393 A (NISHIMURA et al) 16 June 1998, see entire document.	1-12



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

07 MARCH 2000

Date of mailing of the international search report

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Facsimile No. (703) 305-3230

Authorized officer *Jim Park*

DAE YOUNG LEE

Telephone No. (703) 305-0393

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/01929

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,559,193 A (OGAWA et al) 17 December 1985, see entire document.	1-12